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[6]We use the set of units $\hbar = 2m = \frac{1}{2}e^2 = 1$.
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Eigenvalues of the $2p3p\ ^3P$ and $2p3d\ ^{1,3}D$ Bound States of the Helium Isoelectronic Sequence

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The $1/Z$ expansion method is used to calculate the eigenvalues of the $2p3p\ ^3P$ and $2p3d\ ^{1,3}D$ states of the helium isoelectronic sequence. The results are compared to variational calculations for neutral helium. Wavelengths are predicted for a number of transitions originating in doubly excited states of the heliumlike ions up to Fe XXV. The results for neutral helium are compared to recent beam-foil experiments and alternative line identifications are made. The predicted wavelength for the $2p3d\ ^3D - 2p^2\ ^3P$ transition is 3014 Å, in close agreement with the line observed by Berry *et al.* at 3012 ± 2 Å.

I. INTRODUCTION

The existence of doubly excited states in neutral helium has been known for many years through studies of the helium arc spectrum[1,2] and the energy-loss spectrum in electron-helium scattering.[3] States such as the $2pnl\ ^{1,3}L$ sequence give rise to sharp spectral lines since they are prevented from autoionizing by parity and angular-momentum selection rules. Recent studies of these states by the trapped-electron method[4] and beam-foil spectroscopy[5,6] emphasize the need for accurate calculations of their positions and radiative lifetimes. In addition, lines involving doubly excited states of the heliumlike ions have been observed in solar flares[7] and the solar corona.[8]

The $2p^2\ ^3P$ state has been studied by several authors.[9–12] The most extensive calculations by Aashamar,[10] including mass polarization and relativistic effects, predict a $2p^2\ ^3P - 1s2p\ ^3P$ transition frequency of 312 217 cm^{-1} in slight disagreement with the old experimental value, 312 118 cm^{-1},[2] but in agreement with the new value of 312 214 cm^{-1}.[13] The $2p3p\ ^1P$ states of the helium sequence have been studied by Drake and Dalgarno.[11]

In this paper, the $1/Z$ expansion perturbation method is applied to the bound $2p3d\ ^{1,3}D$ and $2p3p\ ^3P$ states of the helium sequence. Wavelengths are predicted for transitions originating from the doubly excited states for the heliumlike ions with $Z \leq 26$ (Fe XXV). Variational calculations for neutral helium are presented as a check on the accuracy of the perturbation expansion. The results suggest that the line observed by Berry *et al.* at 306 ± 1 Å is the $2p3d\ ^1D - 1s3d\ ^1D$ transition ($\lambda = 305.4$ Å).

II. 1/Z EXPANSION METHOD

An accurate and efficient method of generating wave functions for the entire helium isoelectronic sequence is provided by the Hylleraas-Scherr-Knight variation-perturbation procedure.[14] The Schrödinger equation to be solved is

$$(H - E)\Psi = 0 , \tag{1}$$

where

$$H = H_0 + Z^{-1}V_{12} , \tag{2}$$

$$H_0 = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 , \tag{3}$$

$$V_{12} = 1/r_{12} . \tag{4}$$

The unit of energy is Z^2 a.u., and the unit of length is $Z^{-1}\,a_0$. Introducing the perturbation expansions

TABLE I. Energy expansion coefficients (a.u.).

Order	$2p3p\ ^3P$	$2p3d\ ^1D$	$2p3d\ ^3D$
0	−0.180 555 6	−0.180 555 6	−0.180 555 6
1	+0.096 412 1	+0.093 299 9	+0.104 511 3
2	−0.036 770 2	−0.024 579 0	−0.044 901 4
3	−0.002 399 5	−0.004 018 1	−0.001 832 9
4	−0.002 943 1	−0.003 799 8	−0.001 377 6
5	+0.001 057 9	−0.003 149 3	+0.000 411 7
6	+0.002 332 8	−0.002 516 0	+0.000 593 0
7	+0.001 465 1	−0.001 963 5	−0.000 697 2
8	−0.000 379 7	−0.001 398 5	−0.001 486 1
9	−0.002 078 2	−0.000 866 1	−0.001 290 9

$$\Psi = \Psi_0 + \sum_{n=1}^{\infty} \Psi_n Z^{-n} \ , \tag{5}$$

$$E = E_0 + \sum_{n=1}^{\infty} E_n Z^{-n} \ , \tag{6}$$

the zero-order function satisfies the hydrogenic equation

$$(H_0 - E_0)\Psi_0 = 0 \ , \tag{7}$$

and the Ψ_n, $n > 0$, satisfy a series of perturbation equations which are often solved by finding the stationary values of the functionals[10]

$$J_n = \langle n | H_0 - E_0 | n \rangle + 2\langle n | V_{12} - E_1 | n-1 \rangle - \sum_{k=2}^{2n} E_k \sum_{i=n-k}^{n} \langle i | 2n-k-i \rangle \tag{8}$$

with respect to arbitrary variations of the Ψ_n, assuming that all the Ψ_m with $m < n$ are known exactly.

In the formulation of Dalgarno and Drake, [15] a set of M orthonormal functions ϕ_i is introduced, each of which is constructed from a linear combination of M functions of the form

$$x_j = (1 \pm P_{12}) r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} \mathcal{Y}^M_{L l_1 l_2}(\hat{r}_1, \hat{r}_2) \ , \tag{9}$$

where

$$\mathcal{Y}^M_{L l_1 l_2}(\hat{r}_1, \hat{r}_2) = \sum_{m_1 m_2} \langle l_1 m_1 l_2 m_2 | LM \rangle Y^{m_1}_{l_1}(\hat{r}_1) Y^{m_2}_{l_2}(\hat{r}_2) \tag{10}$$

and satisfies

$$\langle \phi_i | H_0 | \phi_j \rangle = \epsilon_i \delta_{ij} \ . \tag{11}$$

TABLE III. $1/Z$ expansion eigenvalues for the helium sequence (a.u.).

Z	$2p3p\ ^1P$	$2p3p\ ^3P$	$2p3d\ ^1D$	$2p3d\ ^3D$
2	−0.580 245	−0.567 802	−0.563 801	−0.559 328 5
3	−1.401 411	−1.373 588	−1.371 599	−1.357 114 5
4	−2.583 994	−2.540 768	−2.541 572	−2.516 281 8
5	−4.127 776	−4.069 184	−4.072 954	−4.036 651 6
6	−6.032 706	−5.958 772	−5.965 572	−5.918 175 2
7	−8.298 766	−8.209 506	−8.219 364	−8.160 833 2
8	−10.925 949	−10.821 372	−10.834 304	−10.764 616
9	−13.914 248	−13.794 363	−13.810 378	−13.729 520
10	−17.263 664	−17.128 473	−17.147 579	−17.055 541
11	−20.974 194	−20.823 701	−20.845 901	−20.742 677
12	−25.045 838	−24.880 045	−24.905 343	−24.790 928
13	−29.478 594	−29.297 504	−29.325 902	−29.200 293
14	−34.272 463	−34.076 076	−34.107 577	−33.970 770
15	−39.427 444	−39.215 762	−39.250 367	−39.102 360
16	−44.943 537	−44.716 561	−44.754 269	−44.595 063
17	−50.820 741	−50.578 472	−50.619 286	−50.448 878
18	−57.059 058	−56.801 496	−56.845 416	−56.663 804
19	−63.658 486	−63.385 631	−63.432 659	−63.239 843
20	−70.619 025	−70.330 879	−70.381 014	−70.176 993
21	−77.940 676	−77.637 238	−77.690 481	−77.475 255
22	−85.623 439	−85.304 709	−85.361 061	−85.134 628
23	−93.667 313	−93.333 292	−93.392 752	−93.155 113
24	−102.072 30	−101.722 99	−101.785 56	−101.536 71
25	−110.083 84	−110.473 79	−110.539 47	−110.279 42
26	−119.965 60	−119.585 71	−119.654 50	−119.383 24

P_{12} indicates the interchange of labels 1 and 2 in (9), with the (+) sign referring to singlet states and the (−) sign to triplet states. The scale factors α and β are set equal to their hydrogenic values; for example, $\alpha = \frac{1}{2}$ and $\beta = \frac{1}{3}$ for the $2p3d\ ^{1,3}D$ states. Then one of the ϕ_i, say ϕ_s, is the exact hydrogenic Ψ_0 with $\epsilon_s = E_0$, and the remaining basis functions ϕ_i $(i \neq s)$ form a synthetic representation of the spectrum of H_0. If we expand Ψ_n in the finite basis set

$$\Psi_n = \sum_{i \neq s}^{M} a_i^{(n)} \phi_i \tag{12}$$

and evaluate J_n, demanding that its value be stationary with respect to variations of the $a_i^{(n)}$, then Ψ_n and E_n are determined by the recursion relations

$$\langle \Psi_n | = \sum_{i \neq s}^{M} \left(\frac{\langle \phi_i | V_{12} | \Psi_{n-1} \rangle}{\epsilon_s - \epsilon_i} \langle \phi_i | - \sum_{p=1}^{n-1} E_p \frac{\langle \phi_i | \Psi_{n-p} \rangle}{\epsilon_s - \epsilon_i} \langle \phi_i | \right) \tag{13}$$

TABLE II. Variational eigenvalues for helium (a.u.).

	$2p3p\ ^1P$	$2p3p\ ^3P$	$2p3d\ ^1D$	$2p3d\ ^3D$
β_{opt}	0.54	0.54	0.51	0.49
$E_{var}(20)$	−0.580 245 638 7	−0.567 762 03	−0.563 785 56	−0.559 325 60
$E_{var}(30)$	−0.580 246 438 4	−0.567 810 08	−0.563 799 56	−0.559 327 40
$E_{var}(40)$	−0.580 246 460 8	−0.567 811 07	−0.563 800 10	−0.559 327 82
$E_{var}(50)$	−0.580 246 463 6	−0.567 811 30	−0.563 800 23	−0.559 328 04
$E(Z$ expan.)	−0.580 245	−0.567 802	−0.563 801	−0.559 328 5

and

$$E_n = \langle \Psi_{n-1} | V_{12} | \Psi_0 \rangle - \sum_{p=1}^{n-1} E_p \langle \Psi_{n-p} | \Psi_0 \rangle \ . \qquad (14)$$

With a finite basis set, the above equations provide approximations to Ψ_n and E_n (but not bounds) up to some finite order. Since the accuracy almost certainly increases with increasing Z, a variational bound calculation for $Z=2$ was performed to establish the accuracy of the nonrelativistic eigenvalues for the entire isoelectronic sequence. The results of the variational and $1/Z$ expansion calculations are given in Sec. III.

III. EIGENVALUES AND PREDICTED WAVELENGTHS

Wave functions for the helium isoelectronic sequence were constructed from (13) and (14), using 50-term basis sets.

The $1/Z$ expansion coefficients for the $2p3p\,^3P$, $2p3d\,^1D$, and $2p3d\,^3D$ eigenvalues are given through 9th order in Table I. The series was arbitrarily truncated at 9th order because the higher-order coefficients are unreliable with this size basis sets. The coefficients for the $2p3p\,^1P$ state were listed previously by Drake and Dalgarno.[11]

The expansions summed through 9th order for neutral helium are compared with variational calculations in Table II. The variational basis sets contain 20, 30, 40, and 50 terms. In each case, we set $\alpha=1$ and minimized the energy with respect to β for the 50-term basis set. The optimized values of β are also given in Table II. The comparison indicates the number of figures after the decimal that are reliable in the $1/Z$ expansion eigenvalues for the remainder of the isoelectronic sequence. The latter eigenvalues, summed through 9th order, are listed in Table III. For large Z, relativistic corrections should also be included. We give in Table IV the predicted nonrelativistic wavelengths for several transitions, using the variational eigenvalues for neutral helium where available.

IV. DISCUSSION

Berry *et al.*[6] have tentatively identified their 306 ± 1 Å line as the helium $2p3p\,^3P$–$1s3p\,^3P$ transition with a theoretical wavelength of 305.8 Å. However they did not observe the companion $2p3p\,^3P$–$1s2p\,^3P$ transition at 291.1 Å, thus casting doubt on the identification. Both transitions involve one-electron jumps and should be of comparable intensity. Our results show that the observed line could equally well be the $2p3d\,^1D$–$1s3d\,^1D$ transition expected to lie at 305.4 Å. In addition, the $2p3d\,^3D$–$2p^2\,^3P$ transition wavelength is predicted to be 3014 Å. In unpublished work,[16] a line has been observed at 3012 ± 2 Å in harmony with the predicted wavelength. If our identification is correct, then theirs is the first observation of the $2p3d\,^3D$ state. A weak line was also observed

TABLE IV. Wavelengths of transitions in the helium isoelectronic series (in Å).[a,b]

Z	$1s2p\,^3P$–$2p^2\,^3P$	$1s2p\,^3P$–$2p3p\,^3P$	$1s2p\,^1P$–$2p3p\,^1P$	$1s3p\,^3P$–$2p^2\,^3P$	$1s3p\,^3P$–$2p3p\,^3P$	$1s3p\,^1P$–$2p3p\,^1P$
2	320.27	291.07	295.18	338.11	305.74	308.93
3	141.02	124.69	126.84	155.3	135.8	137.3
4	78.66	68.68	69.80	88.79	76.27	77.07
5	50.05	43.38	44.02	57.38	48.78	49.23
6	34.60	29.85	30.25	40.10	33.86	34.13
7	25.34	21.79	22.05	29.60	24.86	25.05
8	19.35	16.60	16.78	22.74	19.03	19.16
9	15.26	13.07	13.20	18.02	15.03	15.12
10	12.34	10.55	10.65	14.62	12.17	12.24
11	10.19	8.70	8.77	12.11	10.06	10.11
12	8.55	7.29	7.35	10.19	8.45	8.49
13	7.28	6.20	6.25	8.69	7.20	7.23
14	6.27	5.34	5.38	7.50	6.21	6.23
15	5.46	4.64	4.68	6.54	5.41	5.43
16	4.79	4.08	4.10	5.75	4.75	4.77
17	4.24	3.61	3.63	5.10	4.21	4.22
18	3.78	3.22	3.23	4.55	3.75	3.77
19	3.39	2.88	2.90	4.09	3.37	3.38
20	3.06	2.60	2.61	3.69	3.04	3.05
21	2.78	2.36	2.37	3.35	2.76	2.77
22	2.53	2.15	2.16	3.05	2.51	2.52
23	2.31	1.96	1.97	2.80	2.30	2.30
24	2.12	1.80	1.81	2.57	2.11	2.12
25	1.96	1.66	1.67	2.37	1.95	1.95
26	1.81	1.53	1.54	2.19	1.80	1.80

Z	$1s3d\,^3D$–$2p3d\,^3D$	$1s3d\,^1D$–$2p3d\,^1D$	$2s2p\,^3P$–$2p^2\,^3P$	$2s2p\,^3P$–$2p3p\,^3P$	$2s2p\,^1P$–$2p3p\,^1P$	$2p^2\,^3P$–$2p3d\,^3D$
2	304.5[c]	305.4[c]	9099.93	2363.75	4021.78	3014.01
3	135.38	135.98	5584.	902.85	1276.	1036.6
4	76.14	76.47	4032.6	477.14	618.55	525.87
5	48.71	48.91	3157.1	295.13	363.42	318.16
6	33.82	33.94	2594.4	200.58	238.67	213.26
7	24.84	24.92	2202.1	145.19	168.58	152.90
8	19.02	19.07	1912.9	109.96	125.34	115.00
9	15.02	15.06	1690.9	86.17	96.82	89.64
10	12.17	12.20	1515.1	69.34	77.02	71.83
11	10.05	10.08	1372.4	57.01	62.72	58.85
12	8.45	8.47	1254.3	47.69	52.06	49.10
13	7.20	7.21	1154.9	40.49	43.90	41.59
14	6.21	6.22	1070.1	34.80	37.52	35.68
15	5.41	5.42	996.93	30.24	32.44	30.94
16	4.75	4.76	933.11	26.51	28.32	27.09
17	4.21	4.21	876.98	23.44	24.94	23.92
18	3.75	3.76	827.21	20.87	22.13	21.27
19	3.37	3.37	782.79	18.70	19.77	19.04
20	3.04	3.04	742.90	16.85	17.76	17.14
21	2.76	2.76	706.88	15.26	16.05	15.51
22	2.51	2.52	674.19	13.89	14.57	14.11
23	2.30	2.30	644.39	12.70	13.29	12.89
24	2.11	2.11	617.12	11.65	12.17	11.81
25	1.95	1.95	592.05	10.72	11.19	10.87
26	1.80	1.80	568.95	9.91	10.32	10.04

[a] These wavelengths were calculated using a value of 109 737.31 cm^{-1} for Rydberg's constant.

[b] $1s2p$ and $1s3p$ states for helium were obtained from Schiff, Lifson, Pekeris, and Rabinowitz, Phys. Rev. 140, A1104 (1965); the $2p^2\,^3P$ state from Ref. 10; the $2p3p\,^1P$ state from Ref. 11; the $1s3d$ states from Ref. 15; and the $2s2p$ states from G. W. F. Drake and A. Dalgarno, Proc. Roy. Soc. (London) A320, 549 (1971).

[c] Wavelength calculated from $1/Z$ expansion energy for $1s3d$ states for helium.

at 2365 ± 5 Å, corresponding well to the $2s2p\ ^3P$–$1s3d\ ^1D$ transition predicted to be 2364 Å.

Calculations of the oscillator strengths for these transitions are in progress.

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Permutation Symmetry and the N-Electron Problem

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The techniques of tensor algebra customarily applied to exploit spatial symmetry are applied to exploit permutational symmetry of the N-electron problem. In the approximation of no spin-orbit coupling, the results are nontrivial and give a further reduction of what is normally regarded as the reduced matrix element with respect to spatial symmetry alone. The required 3-j coefficients of the permutation group are evaluated in an appendix so that intermediate group-theoretical indices that have no direct physical significance are eliminated from the formulation. The spin integral for any operator can always be reduced to known integrals of the fundamental Pauli operators. Thus all matrix elements can be reduced to a corresponding spin-free form with known weighting coefficients. An explicit expression is given for the matrix element of an operator suitable for evaluating spin–own-orbit coupling or spin density at the nucleus. A recursion relation for the Clebsch-Gordan coefficients of bipartition representations of S_N in terms of its subgroups and the 9-j sympols of $SU(2)$ is developed in the appendix. For one of the representations being the totally symmetric representation, the Clebsch-Gordan coefficient is known and the recursion relation (the group-orthogonality relation in this case) can be considered as giving nontrivial sum rules on the 9-j symbols of $SU(2)$.

I. INTRODUCTION

In most atomic, molecular, and solid-state electron problems one is interested, at least as a zero-order approximation, in the solutions of a Hamiltonian for N interacting indistinguishable Fermions having no direct spin-orbit interaction. Not only do the permutations of the particle spin and orbit coordinates commute with the Hamiltonian, but the direct-product permutations of the spin and orbit coordinates considered separately also commute with the Hamiltonian. It follows from the theory of group representations that the eigensolutions of the model Hamiltonian are characterized by the irreducible representations of the symmetric group on N particles in spin and orbit space separately. If the spin basis is restricted to Nth-rank products of the one-particle two-dimensional basis, then the admissible spin irreducible representations are limited to those connected with the bipartitions of N determined by the total spin value S, viz., $[\frac{1}{2}N + S, \frac{1}{2}N - S]$. The admissible orbital irreducible